
Preparation and characterisation of Pd nanoparticles doped UO_2 samples

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Abstract: To assess the safety of the deep geological disposal that would store the spent nuclear fuel (SNF), studies are centred on the SNF behaviour under repository conditions. UO_2 , which is the most common compound of SNF matrix, is highly sensitive to the redox potential and it could be oxidised to more soluble phases, enhancing the liberation of harmful radionuclides. Among fission products in the SNF, ϵ -particles (nanoparticles) are believed to play an important role avoiding the oxidation. Consequently, scientists are testing efficient and low cost methodologies for the preparation of novel materials by incorporation of nanoparticles into bulk components. In this communication we present the methodology for preparation of non-irradiated UO_2 doped with Pd Nanoparticles (Pd-NPs), as an analogue of ϵ -particles present in the SNF. Pd-NPs doped UO_2 samples were characterised by high resolution electron microscopy to identify the presence, the morphology and distribution of the nanoparticles.

Keywords: uranium oxide; palladium nanoparticles; nanotechnology; spent nuclear fuel; sample characterisation.

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1 Introduction

The most widely accepted management solution for spent nuclear fuel (SNF) is its location in a deep geological repository (DGR). DGR is based on a multibarrier concept. The DGR needs to be designed in a way that the multiple barriers guarantee that the waste that eventually might reach the biosphere will always be below the accepted levels and, therefore, won't have any significant impact. To be able to predict its future behaviour, it is mandatory to evaluate the possible reactions in which SNF could be involved under repository conditions. Regarding this, non-irradiated UO₂ has been widely used as a chemical analogue of UO₂ based nuclear fuels.

The most conservative projections used in performance assessment exercises consider a minimum of 1000 years until a defective canister breaks and water comes into contact with the fuel. At this situation, there will be a series of steps or reactions between the SNF and water (water radiolysis, fuel oxidation, fuel dissolution and precipitation of secondary phases, etc.) [1,2]. Each stage may differ depending on various key parameters such as pH, pe, temperature, composition of water and pressure among many others. Different redox active chemical species are involved in this stage, both oxidants (H₂O₂, O₂) and reducing (H₂), formed by alpha-radiolysis of water molecules owing to the alpha radiation emitted by the SNF [3–6].

During the irradiation process, UO₂ individual grains grow, followed by the appearance of non-volatile fission products mainly located at the grain boundaries [2]. Some of these fission products are found in SNF forming metallic particles (of special interest the particles containing Pd, Pt and Rh) segregated from the UO₂ matrix. They are known as ϵ -particles.

Under the expected deep geological disposal conditions, those particles can act as catalysers, enhance the reactivity of reducing species and, therefore, counteract the effects of oxidants. The effect of these ϵ -particles could then prevent the oxidation of the UO₂ matrix to more soluble solid phases.

To study the effect of these particles, UO₂ samples were doped with palladium by using the doping immersion method to produce nanoparticles (Pd-NPs) as ϵ -particles analogues present in the irradiated SNF. Nanoparticles (NPs) represent an alternative to conventional materials owing to the increase of their exposed surface area. For Pd-NPs, we have the assumption that nanometric scale substantially enhances the efficiency catalytic effect to prevent oxidation of UO₂; as these NPs have proven enhanced catalytic activity and gas storage [7]. The preparation and characterisation of these samples are presented in this work.

2 Experimental methods

2.1 Materials and reagents

Hydrochloric acid and palladium (II) chloride from Sigma Aldrich p.a. grade were used as received. Non-irradiated UO₂ particles from synthetic uranium dioxide provided by ENUSA (Empresa Nacional del Uranio S.A., Spain) with a diameter lower than 75 μ m were used to synthesise the Pd-NPs.

2.2 Preparation of Pd-NPs doped UO₂ samples

A specific amount of PdCl₂ was dissolved in HCl/H₂O solution (under volumetric proportions of 1.4/100 per each gram of PdCl₂). Once the Pd was dissolved, the solution is added to a specific amount of UO₂. Thus, the dissolution was added to the solid drop by drop until the solid is saturated with liquid and the mixture is dried. This last step was repeated until the all dissolution was added to the solid. Finally, the sample was introduced into an oven and the temperature was maintained to 350°C for 24 h.

2.3 Sample characterisation by electron microscopy

Approximately 1 mg of Pd-NPs doped UO_2 sample was dispersed in 5 mL of acetone as organic solvent and then placed in an ultrasound bath for 1 h. Finally, a drop of the suspension was placed on a grid and allowed to dry before both high resolution transmission electron microscopy (HR-TEM) and energy dispersive X-ray spectroscopy (EDS) analysis.

HR-TEM images and EDS analysis were obtained using a JEM-2011 unit with an acceleration voltage of 200 kV. Further Scanning Transmission Microscopy Images (S/TEM) and corresponding EDS analyses were obtained with a FEI Tecnai F20 S/TEM microscope with acceleration voltage of 200 kV.

3 Results and discussion

The advances of materials science have involved the improvement of characterisation techniques to satisfy the necessity of a better understanding of the structure-properties relation in novel materials. After the design and preparation of a novel material such as Pd-NPs doped UO_2 , the next step is the full characterisation of its principal features, such as: NPs size and distribution, chemical composition, morphology and special effects given by these nanometric particles.

Firstly the electron microscopy characterisation was carried out in transmission mode, where the dark zones are the ones with interest of study (see Figure 1(a)). Subsequently, S/TEM characterisation was carried out for the samples. In scanning mode, the clear (white) zones represent the actual material of interest (see Figure 1(b)) which in this case was mainly UO_2 . This dual mode analysis made feasible the location of Pd-NPs, seeming to have spherical morphology and arranged mainly on the surface of the UO_2 , as the ϵ particles do on the actual SNF [2]. EDS allows obtaining qualitative information about the chemical composition and location of the elements present in the sample. The EDS spectra for Pd-NPs can be seen in Figures 1(b) and (c), showing the presence of nanometric Pd.

Figure 2(a) shows the zone selected for EDS-line mapping of the doped sample as supplementary data for the qualitative identification of Pd and U in the samples. From EDS-line mapping data is possible to have precise information of the spatial location of the elements. Several regions can be observed in the EDS scan:

- the first region where there is only Pd signal (Figure 2(b))
- a second region where only U was detected (see Figure 2(c)).

Clearly, the U signal goes from the point when the Pd-NP ends to the end of the line scanned.

Further research using different analytical methods will be carried out to obtain the surface Pd-/U atomic ratio and the oxidation states for both elements in the doped samples. Such techniques will be: X-ray photoelectron spectroscopy (XPS) [8] and electron energy loss spectroscopy (EELS) [7,8], this last technique with a higher spatial resolution than the others. This is because EELS takes advantage of the resolution offered by TEM, which provides the possibility of elemental analysis with spatial resolution at nanometric scale [9,10]. This can be seen in the LineScan (red line)

presented in Figure 2(a), with a 250 nm length with a capitation rate of 1 nm; which means that elemental analysis is carried out per nm (Figures 2(b) and (c)).

A highly sensitive and specific analysis of both uranium and palladium oxidation states could be accomplished by X-ray absorption spectroscopy (XAS) in a synchrotron facility [11–13]. XAS is a powerful structural technique to investigate and specifically characterise the electronic states and local structure around impurities and/or trace elements in samples of interest. In addition, the resolution that could be achieved by synchrotron radiation could overcome the issues presented with previously used techniques for the characterisation of oxidation states. For instance, the use of a non-monochromatic source decreases the sensitivity and specificity of the analysis.

Figure 1 HR-TEM image (a) S/TEM image (b) of Pd-NPs doped UO_2 samples with the corresponding EDS spectra (indicated as a red circle in (b) verifying the presence of Pd at nanometric scale (c) (see online version for colours)

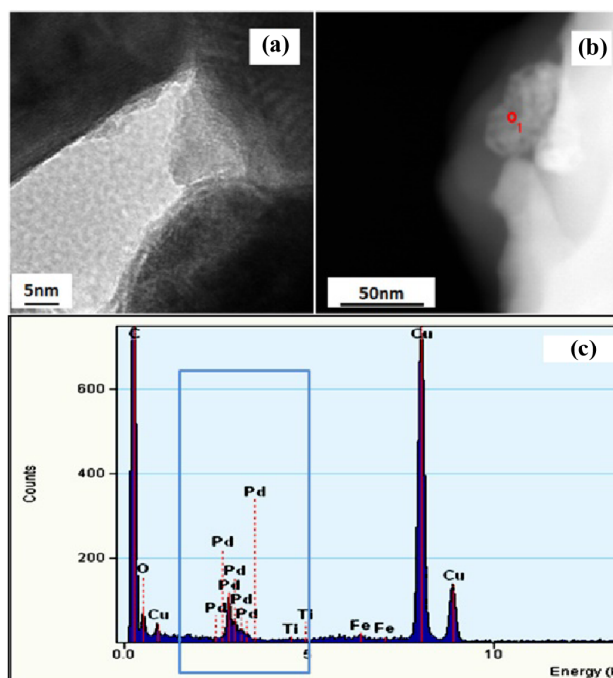
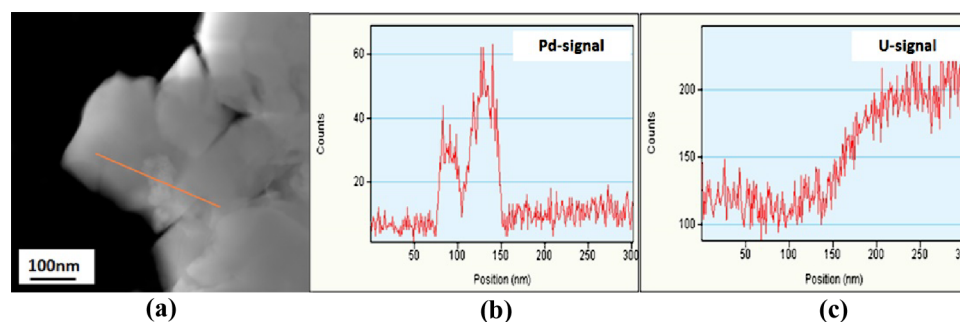


Figure 2 EDS LineScan of Pd-NPs doped UO_2 sample (a) confirming the presence and distribution of Pd (b) and U (c) (see online version for colours)



4 Conclusions

The research presented has particular emphasis in the surface doping of UO_2 with Pd-NPs and the characterisation of the resulting material with electron microscopy. Thus, it can be said that Pd-NPs have been successfully prepared on the UO_2 powder by using the immersion doping method. Pd-NPs have been observed to be near to 50 nm diameter Figures 1 and 2, as can be observed in both S/TEM and HR-TEM images. This is conclusive evidence that Pd-NPs can be obtained and is being used as an analogue of ϵ particles in the SNF. Experiments are being started with these doped samples in order to ascertain the role that ϵ -particles may take in the prevention of UO_2 oxidation in the presence of both reducing and oxidising species, under representative repository near field conditions. Thus, more detailed analysis of the oxidation states of uranium will be studied by XPS, EELS and XAS.

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